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Chemical properties of heavy metals in typical hospital waste incinerator ashes in China

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ABSTRACT

Incineration has become the main mechanism for hospital waste (HW) disposal in China after the outbreak of Severe Acute Respiratory Syndrome (SARS) in 2003. However, little information is available on the chemical properties of the resulting ashes. In the present study, 22 HW ash samples, including 14 samples of bottom ash and eight samples of fly ash, were collected from four typical HW incineration plants located across China. Chemical analysis indicated that the HW ashes contained large amounts of metal salts of Al, Ca, Fe, K, Mg, Na with a concentration range of 1.8–315 g kg⁻¹. Furthermore, the ashes contained high concentrations of heavy metals such as Ag, As, Ba, Bi, Cd, Cr, Cu, Mn, Ni, Pb, Ti, Sb, Sn, Sr, Zn with a vast range of 1.1–121,411 mg kg⁻¹, with higher concentrations found in the fly ash samples. Sequential extraction results showed that Ba, Cr, Ni and Sn are present in the residual fraction, while Cd existed in the exchangeable and carbonate fractions. As, Mn, Zn existed in the Fe–Mn oxide fraction, Pb was present in the Fe–Mn oxide and residual fractions, and Cu was present in the organic matter fraction. Furthermore, toxicity characteristic leaching procedure (TCLP) results indicated that leached amounts of Cd, Cu and Pb from almost all fly ash samples exceeded the USEPA regulated levels. A comparison between the HW ashes and municipal solid waste (MSW) ash showed that both HW bottom ash and fly ash contained higher concentrations of Ag, As, Bi, Cd, Cr, Cu, Pb, Ti, and Zn. This research provides critical information for appropriate HW incineration ash management plans.

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1. Introduction

In China, the generation of hospital waste (HW) has increased rapidly over the past decade. Currently approximately 0.65 million tons of HW are produced every year (Liu et al., 2006). The universal use of disposable plastic and/or metallic appliances during medical treatments is a significant contribution to the total HW generated.

Nevertheless, little attention was paid to the treatment of HW in China before the outbreak of the national-wide Severe Acute Respiratory Syndrome (SARS) in 2003. Most of these wastes were mixed with municipal solid wastes (MSW) for landfilling, and only small amount was treated by steam sterilization to control highly infectious matter (Ji, 2005). A large amount of dangerous infectious HW, especially plastic syringes and needles, were transferred into society without any treatment. Several accidents have been reported where mishandling of HW wastes led to infections (Shang and Jia, 2002). Furthermore, some plastic appliances were even used as recycled material to produce products such as beverage bottles, disposable cups and food bags (Zhang, 2006), which may pose threats to human health.

In 2003, the national-wide SARS outbreak caused the Chinese government to pay greater attention to the handling and disposal of these types of special wastes. Presently, HW is listed as the number one hazardous waste and, furthermore, several regulations on the collection, transportation and disposal of HW have been established by the State Environmental Protection Administration of China. Meanwhile, the government has provided large amounts of funds to support building large- or medium-scale incineration plants for HW disposal. Currently, incineration has become the major method for HW disposal, and almost every big city owns at least one HW incineration plant. It is estimated that currently there are over 300 incinerators and the number is still increasing (Yan et al., 2003). Nevertheless, there are still small-scale incinerators operating in hospitals in some small cities. These types of incinerators may cause special environmental concern.

Generally, in China, a large-scale incineration plant can dispose approximately 30–40 tons of HW per day, and a medium-scale plant can dispose about 20 tons. Thus, large amounts of various HW incineration ashes are generated. Currently, only small amounts of these ashes are solidified by mixing with cement, and a large portion is still disposed by landfilling directly or piling up near the incineration plants.

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Few reports are available on HW ash; most of the studies have focused on the emissions of organic pollutants during the incineration process. It has been reported that when some plastics in HW are incinerated, carcinogenic chemicals such as PAHs (polycyclic aromatic hydrocarbons), PCBs (polychlorinated biphenyls), PCDDs (polychlorinated dibenzo *p*-dioxins) and PCDFs (polychlorinated dibenzofurans) can be produced and deposited on the surface of the ash particles (Wagner and Green, 1993; Lee et al., 2002). Kuo et al. (1999) has shown that high concentrations of Cr and Ni in HW bottom ash were found because most hospitals in Taiwan do not grind or melt needles and syringes. For comparisons, the concentration of Cr in HW ash was 17 times higher than that typically found in MSW ashes. Meanwhile, high mobility of heavy metals such as Cd, Ni, Pb and Zn in HW ash was also reported since these elements are mainly contained in exchangeable and carbonate forms (Lombardi et al., 1998; Sukandar et al., 2006; Ibanez et al., 2000).

The main objectives of this work were: (1) to examine the chemical composition, especially heavy metal concentrations, in HW ashes; (2) to identify the heavy metal species to investigate their environmental mobility and availability; and (3) to determine the leachability of heavy metals in HW ashes to evaluate their environmental impacts.

2. Materials and methods

2.1. Sample collection and preparation

Twenty-two HW ash samples were collected from four typical hospital waste incinerators in China. Sampling locations are presented in Fig. 1. Table 1 shows the background information and operating conditions of the incinerators. HWI-I, located in south China, is a special type of medium-scale incinerator, which combined more than ten small fixed grate furnaces. Part or all of the furnaces are operated according to the amount of hospital wastes collected. Although, air pollution control devices (APCDs) are equipped on each furnace, fly ash could not be collected in this type of incinerator; thus only bottom ash was obtained. Two mixed

samples (BA1, BA2) were collected every two weeks from the incinerator. HWI-II is a typical small incinerator run by a hospital in a county located in the central part of China (Fig. 1). The incinerator, representing hundreds of incinerators running in China, has no APCDs, thus only bottom ash could be collected. Sampling activities were conducted over three months, and 12 mixed samples (BA3–BA14) were collected once a week. HWI-III, located in northeast China, is a medium-scale incinerator operated in a large city. Incineration ash is mainly collected in the bag filters as fly ash, and the residue mainly consists of unburned glass, plastics and metallic matter. Thus, only fly ash samples were collected from these incinerators. The sampling activities were carried out with for one month, and two homogenized samples (FA1, FA2) were collected. HWI-IV, located in the capital city, Beijing, is a large-scale incinerator with a batch processing capacity of 40 tons per day; the incinerator was properly designed and has well-maintained APCDs. Six samples (FA3–FA8) were collected twice a month. After sampling, all samples were dried at 105 °C for 24 h and ground to <0.25 mm using an agate mortar for analysis.

Table 1

Specified operating conditions of the hospital waste incinerators investigated in this study

Condition	HWI-I	HWI-II	HWI-III	HWI-IV
Type of incinerator	Medium-scale	Small-scale	Medium-scale	Large-scale
Ash type	Bottom ash	Bottom ash	Fly ash	Fly ash
Combustion temperature (°C)				
First combustion chamber	700–800 °C	300–400 °C	500–550 °C	500–600 °C
Second combustion chamber	–	–	900–1000 °C	850–1150 °C
Fuels used	Diesel oil	Diesel oil	Diesel oil and natural gas	Diesel oil

No second combustion chamber.

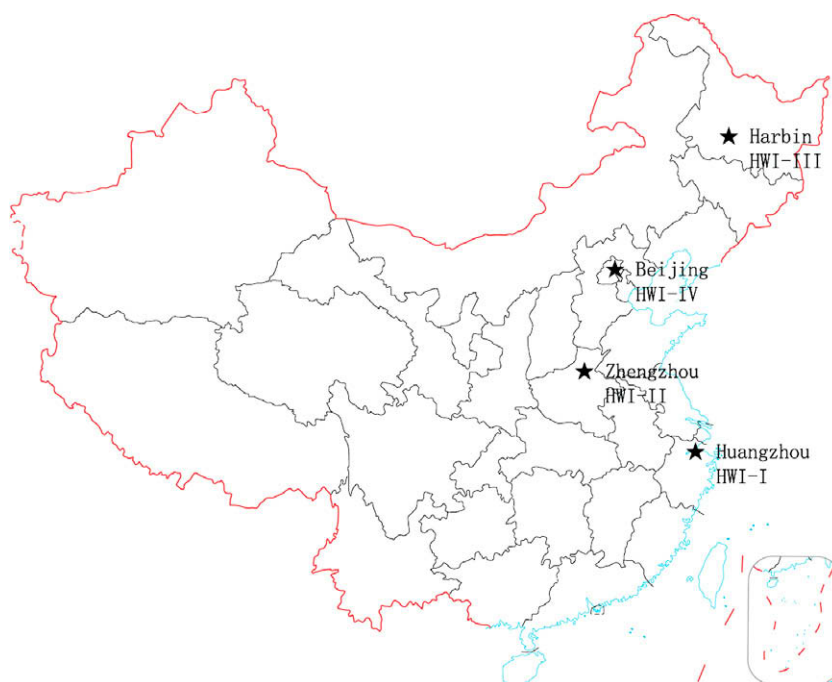


Fig. 1. Map of China showing the sampling locations.

Table 2
Sequential extraction procedure for heavy metals in the HW ashes

Step	Fraction	Reagent/5 g sample	Shaking time and temperature
1	Exchangeable	100 ml 1 M NaOAc (pH 8.2)	1 h at 25 °C
2	Carbonate	100 ml 1 M NaOAc (pH 5.0 adjusted with HOAc)	5 h at 25 °C
3	Fe–Mn oxides	100 ml 0.04 M NH ₂ OH–HCl in 25% (v/v) CH ₃ COOH	5 h at 96 ± 3 °C
4	Organic matters	15 ml 0.02 M HNO ₃ + 25 ml 30% H ₂ O ₂ (pH 2 adjusted with HNO ₃)	2 h at 85 ± 2 °C
		15 ml 30% H ₂ O ₂ (pH 2 adjusted with HNO ₃)	3 h at 85 ± 2 °C
		25 ml 3.2 M CH ₃ COONH ₄ in 20% HNO ₃	30 min at 85 ± 2 °C
5	Residual	Total content minus prior four steps	

2.2. Elemental analysis

Heavy metals were analyzed by inductively coupled plasma optical emission spectroscopy (ICP-OES) after HNO₃/HClO₄/HF digestion (Yamasaki, 1997). Analysis of heavy metals in the ashes was performed using a sequential extraction procedure (SEP) suggested by Tessier et al. (1979) and modified by Tan et al. (1997). The procedure classified elements into five fractions (Table 2). After each extraction, the separation was achieved by centrifuging at 5000 rpm for 30 min and the supernatant was filtered through 0.45-μm membranes and analyzed by ICP-OES.

2.3. Leaching experiment

Leaching of hazardous heavy metals from the ashes was examined according to toxicity characteristic leaching procedure (TCLP, USEPA, 1992), in which two kinds of extraction solutions, i.e., solution # 1 (acetic acid, pH 4.9 ± 0.05) and solution # 2 (acetic acid, pH 2.88 ± 0.05), were used. The liquid-to-solid ratio was 20:1 and agitation time was 18 h with rotary tumbler at 30 ± 2 rpm. After extraction, the leachates were filtered with Whatman GF/C glass fiber filter paper. The leachate was acidified with 1 M HNO₃ solution and subjected to ICP-OES analysis.

2.4. Quality control

The quality and precision of metallic element analysis were controlled using the reference material (NIST 1646), which was a sediment from National Institute of Standards and Technology (USA). A comparison between certified values and those found in this study are illustrated in Table 3. The recoveries were between 63% and 140%. Laboratory quality control procedures included sample triplicates. Relative standard deviations of the triplicate analyses were all below 5%. Averages of the triplicates are presented in the tables and figures.

3. Results and discussion

3.1. Metal concentrations in various HW ashes

Metallic element concentrations in the HW ash samples are quite different between bottom ashes (Table 4) and fly ashes (Table 5). The bottom ashes generally contain a high concentration of various metal salts with average values >10 g kg⁻¹, including salts of Ca (89.1–315 g kg⁻¹), Al (18.5–62.9 g kg⁻¹), Mg (10.1–41.5 g kg⁻¹), Na (8.0–26.4 g kg⁻¹), Fe (4.3–52.8 g kg⁻¹) and Zn (2.6–

Table 3
Element analysis of reference material NIST 1646

Metal	Certified value	This study	Recovery (%)
(%)			
Al	2.297% ± 0.018	2.759 ± 0.102	120
Ca	0.519% ± 0.020	0.560 ± 0.050	108
Fe	2.008% ± 0.039	2.141 ± 0.022	107
K	0.864% ± 0.016	1.01 ± 0.098	117
Mg	0.388% ± 0.009	0.429 ± 0.006	110
Na	0.741% ± 0.017	0.758 ± 0.502	102
Ti	0.456% ± 0.021	0.448 ± 0.018	98
(mg kg ⁻¹)			
Ba	210.00	282.39 ± 27.69	134
Co	5.00	7.00 ± 0.83	140
Cr	40.9 ± 1.9	35.7 ± 4.11	87
Cu	10.01 ± 0.34	12.60 ± 0.42	126
Mn	234.5 ± 2.8	214.4 ± 4.11	91
Ni	23.00	29 ± 7.71	130
Pb	11.7 ± 1.2	13.5 ± 2.47	121
V	44.84 ± 0.76	28.08 ± 1.58	63
Zn	48.9 ± 1.6	47.1 ± 1.47	96

30.7 g kg⁻¹). Other abundant elements with average concentrations in the range of 1–10 g kg⁻¹ include K (5.3–19.9 g kg⁻¹), Ti (1.8–15.5 g kg⁻¹), and Ba (0.70–5.1 g kg⁻¹). Most of the toxic heavy metals in the bottom ashes are in the average concentration range of 0.1–10 g kg⁻¹, including Pb (0.07–2.1 g kg⁻¹), Mn (0.24–2.9 g kg⁻¹), Cu (0.07–2.3 g kg⁻¹), Cr (34.4–895 mg kg⁻¹), Sr (164–494 mg kg⁻¹), Sn (170–406 mg kg⁻¹), Ga (69.0–306 mg kg⁻¹), Ni (10.7–667 mg kg⁻¹), Sb (22.8–197 mg kg⁻¹) and Bi (1.1–489 mg kg⁻¹). Other metals, such as Li, As, Co, Ag and Cd were found in minor or trace amounts with concentrations <0.1 g kg⁻¹.

On the other hand, the fly ashes also contain a high content of major metals with average values >10 g kg⁻¹, including Na (36.2–221 mg kg⁻¹), Zn (28.8–121 g kg⁻¹), Ca (21.3–127 g kg⁻¹), K (17.6–37.5 g kg⁻¹), Fe (9.2–29.5 g kg⁻¹) and Mg (3.0–35.6 g kg⁻¹) in abundance order (Table 4). Other metals with average concentrations in the range of 1–10 g kg⁻¹ include Al (1.8–35.9 g kg⁻¹), Pb (0.9–5.4 g kg⁻¹), Ba (1.2–2.9 g kg⁻¹), Ti (0.09–8.9 g kg⁻¹), Cu (0.42–2.9 g kg⁻¹) and Sn (0.59–1.7 g kg⁻¹). Other heavy metals with average concentrations in the range of 0.1–1 g kg⁻¹ include Mn (0.20–0.74 g kg⁻¹), Cd (28.9–635 mg kg⁻¹), As (69.3–237 mg kg⁻¹), Bi (38.9–275 mg kg⁻¹), Sb (87.4–230 mg kg⁻¹), Li (88.9–268 mg kg⁻¹), Sr (87.6–235 mg kg⁻¹), and Ag (40.5–222 mg kg⁻¹). In the fly ashes, Ga, Cr, Ni, Co were found in trace amounts with concentrations <0.1 g kg⁻¹.

As mentioned previously, BA1 and BA2 were from a medium-scale incinerator, while BA3–BA14 was from a small incinerator. It can be seen from Table 4 that metal concentrations in the ash samples generated from the two types of incinerators are quite different. Specifically, the concentrations of Al, Cu, Fe, Ag, Cr, and Ni in BA1 and BA2 were 2.0–2.3, 3.9–15.7, 1.9–11.0, 1.6–10.2, 1.3–15, and 5.7–46.7 times higher than those in BA3–BA14. This could be explained by the fact that the former incinerator (BA1 and BA2) disposed of HW in a big city, including approximately 200 hospitals; thus the HW disposed in this incineration plant contains higher amounts of metallic objects, such as aluminum cans, scalpels, needles, syringes or small metallic medical tools, than the small hospital-run incineration facility. When these metal wastes are incinerated, the ashes are often enriched with metals. Furthermore, it could also be seen that the concentrations of Bi and Pb in BA1 and BA2 are much lower than in BA3–BA14. The possible reason is that the two metals and their associated compounds generally possess high volatility. Since the former incinerator runs at a higher temperature, more Bi and Pb could have volatilized and could be located in the fly ash.

Table 4

Metal concentrations of various HW bottom ash samples

	BA1	BA2	BA3	BA4	BA5	BA6	BA7	BA8	BA9	BA10	BA11	BA12	BA13	BA14
(g kg ⁻¹)														
Al	36.4	62.9	25.7	24.6	18.8	27.7	18.5	23.3	30.2	24.2	27.5	20.6	23.0	25.3
Ba	2.1	1.6	1.7	5.1	2.6	2.1	1.3	0.73	1.4	0.70	1.3	0.82	1.6	1.1
Ca	97.6	186	176	149	140	285	89.1	96.9	140	133	121	315	136	140
Cu	1.1	1.4	0.24	0.17	0.36	0.35	0.16	0.07	0.14	0.07	0.18	0.08	2.3	0.17
Fe	47.5	52.8	27.2	5.9	4.7	11.0	4.3	6.1	4.4	6.0	12.9	9.1	5.8	10.7
K	8.5	6.8	10.3	14.2	9.3	8.1	7.4	19.9	8.4	13.1	10.7	5.3	8.9	11.9
Mg	15.2	19.2	37.3	29.1	22.7	13.6	17.8	16.6	28.0	41.5	21.6	10.1	30.0	34.2
Mn	0.53	1.5	1.1	2.9	0.24	0.36	1.1	0.32	0.39	0.42	0.42	0.32	0.75	0.43
Na	13.1	15.2	17.8	26.4	23.0	11.8	11.0	16.3	12.6	23.2	18.4	8.0	17.5	21.1
Pb	0.33	0.07	1.1	0.95	0.97	0.63	0.88	0.38	2.1	0.52	0.92	0.55	1.4	0.70
Ti	7.1	15.5	7.7	4.9	7.0	2.3	4.7	3.1	7.9	2.7	7.0	1.8	11.4	5.3
Zn	8.4	12.7	8.9	15.8	30.7	16.2	5.9	2.9	18.7	2.6	10.5	23.3	9.1	4.8
(mg kg ⁻¹)														
Ag	24.2	21.4	9.6	4.0	4.7	3.9	2.3	2.1	2.6	6.0	5.4	15.5	3.4	12.3
As	22.1	39.1	14.2	14.3	45.0	50.2	4.9	38.1	20.8	51.0	14.6	30.0	13.4	31.9
Bi	1.1	ND	28.1	53.8	13.2	120	287	73.9	32.2	66.9	29.3	489	ND	36.5
Cd	ND	ND	ND	ND	10.2	1.4	ND	ND	ND	ND	ND	ND	4.2	ND
Co	36.3	49.9	25.9	16.9	20.3	11.5	16.1	12.4	29.5	10.4	23.7	11.1	34.8	18.7
Cr	895	515	313	310	434	709	240	75.8	765	102	352	34.4	643	159
Ga	154	306	181	116	154	75.0	116	92.6	180	84.7	153	69.0	250	151
Li	50.7	76.3	35.8	45.2	55.2	47.0	25.5	32.4	40.8	43.2	44.6	33.0	51.0	37.6
Ni	667	500	41.0	28.6	21.6	31.5	28.0	17.0	23.6	10.7	117	24.1	16.5	20.4
Sb	ND	ND	22.8	50.6	64.6	80.8	127	46.6	63.0	138	197	108	161	183
Sn	368	406	246	170	325	219	245	200	308	211	333	298	400	258
Sr	164	165	409	494	225	484	221	262	261	316	288	394	197	303

All values are the means of triplicate analysis. ND: not detected.

Table 5

Metal concentrations of various HW fly ash samples

	FA1	FA2	FA3	FA4	FA5	FA6	FA7	FA8
(g kg ⁻¹)								
Al	20.7	35.9	2.9	3.2	1.8	6.9	6.3	2.0
Ba	1.4	1.7	2.3	2.6	2.8	1.5	1.2	2.9
Ca	56.4	127	28.7	28.3	24.0	21.3	22.2	27.2
Cu	0.59	0.42	2.1	2.3	2.6	1.5	1.3	2.9
Fe	23.3	29.5	19.0	12.5	12.9	11.1	9.2	13.9
K	17.6	18.4	25.4	27.6	34.9	34.3	31.3	37.5
Mg	35.6	34.6	3.0	3.9	3.9	4.6	4.8	4.7
Mn	0.34	0.74	0.33	0.33	0.40	0.32	0.20	0.61
Na	44.8	36.2	159	189	159	197	221	175
Pb	1.9	0.9	5.3	5.4	4.7	2.7	2.4	5.1
Ti	5.4	8.9	0.12	0.12	0.09	0.39	0.37	0.10
Zn	33.5	28.8	83.7	91.5	115	85.8	70.8	121
(mg kg ⁻¹)								
Ag	69.2	40.5	71.8	102	187	95.0	113	222
As	237	163	166	211	219	69.3	94.8	197
Bi	77.8	38.9	231	235	275	109	76.7	274
Cd	58.7	28.9	635	508	276	103	78.4	211
Co	13.4	23.8	0.58	0.92	1.3	0.82	0.83	1.5
Cr	148	264	28.2	34.7	19.5	5.2	3.5	20.1
Ga	135	192	50.3	49.9	31.8	31.8	30.6	33.8
Li	88.9	146	187	215	208	175	162	268
Ni	36.7	57.3	34.5	35.3	40.6	21.6	20.0	42.1
Sb	87.4	88.8	184	225	230	140	123	224
Sn	928	592	1443	1399	1660	938	906	1328
Sr	102	235	87.6	108	108	109	116	129

All values are the means of triplicate analysis.

Among the fly ash samples, FA1 and FA2 were from a medium-scale incinerator, while FA3–FA8 was from a large-scale incinerator. As can be seen from Table 5, the concentrations of Ca in FA1 and FA2 are much higher than in FA3–FA8, but Na has the opposite trend. This is because the two incinerators employed different reagents for the removal of acidic gases in the incineration process, i.e., FA1/FA2 used Ca(OH)₂ solution while FA3–FA8 used NaOH solutions. Further-

more, it could also be seen from Table 4 that the content of some heavy metals with low thermal mobility such as Ti and Cr could be found enriched in FA1 and FA2, while some high volatilized metals such as Ag, Bi, Cu, Pb, Zn and Cd could be found enriched in FA3–FA8. This could be attributed to the different incineration temperatures performed in the two incinerators, i.e., the FA1/FA2 incinerator performed a lower temperature than FA3–FA8.

Generally, fly ash contains more toxic elements such as As, Cd, Pb, and Zn compared to bottom ash samples. Concentrations of Cd in fly ash samples were about 42–62 times higher than those in bottom ash samples (Tables 4 and 5). Some heavy metals, such as Pb, Zn and Cd, either have high volatility or can easily form high volatile compounds (CdCl₂, ZnCl₂, PbCl₂) (Verhulst et al., 1996; Jung et al., 2004; Shim et al., 2005; Sukandar et al., 2006), and thus tend to be transferred into fly ash during the incineration process. Furthermore, it was also reported that As could be completely volatilized when the incineration temperature was above 650 °C (Verhulst et al., 1996). This could explain the high concentration of As in the fly ash. In contrast, the concentrations of Cr were relatively high in bottom ash samples, which were 3–10 times higher than those in fly ash samples. Cr is generally not thermally mobile during the incineration process, and thus mainly remains in the bottom ash (Jung et al., 2004). In the HW ashes, Ag tends to be enriched in fly ash, probably due to the lower boiling points of silver compounds, e.g., the boiling point of silver nitrate is 440 °C.

Compared to values reported in other literature (Sukandar et al., 2006; Idris and Saed, 2002) for hospital waste incinerator ashes, it is interesting to find that Ba and Zn concentrations in this study are significantly higher, which may be attributed to the difference of raw HW materials. Hospital wastes in China usually contain high amount of plastic matter, while Ba and Zn are usually used as additive in these plastics. For example, PVC used in medical apparatus generally contain these two elements, and this type of plastics also contains high levels of Cl, leading to the high transference rate of Zn into the fly ash because of the formation of ZnCl₂ that has a lower boiling point (732 °C).

3.2. Comparison of metal concentrations in HW ashes and MSW ashes

Metal concentrations in the HW ash were compared with those previously reported in MSW ashes (Herck and Vandecasteele, 2001; Zhang et al., 2002a,b; Zhang and Itoh, 2006; Jung et al., 2004; Wan et al., 2006; Jiang et al., 2004; Song et al., 2004; Wu and Ting, 2006; Shim et al., 2005), so as to identify the metal distribution differences between the two types of ashes (Table 6).

The composition of HW and MSW are quite different. Typically, HW consists of rubber, cotton, syringes, needles, scalpels, metal cans, plastics, glass, and small metallic medical tools, while MSW is generally composed of food scraps, plastics, paper, yard wastes, and minor amounts of household construction materials. Thus the ashes from incineration of the two waste types will be quite different. Table 6 shows that both HW bottom ash and fly ash contain higher amounts of Ag, As, Bi, Ti, and Zn than MSW ashes. Furthermore, HW fly ash contains higher amounts of Cd, Cu, Pb than MSW fly ash, and HW bottom ash contains higher amounts of Cr than MSW bottom ash. In the medical field, these heavy metals are generally used in medicines, photographic materials, and medical tools. Therefore, they are present in the HW waste stream, causing their high concentrations in the resulting incineration ashes. Compounds of As and Ag are usually used in some medicines, and silver nitrate is used as a sensitive material of X-ray plates. Bi is usually added to a sponge for use in surgery or for dressing wounds (Jung et al., 2004). Bi is also used in alloys with Pb, Sn and Cd in the production of small medical tools. High concentrations of Cr may come from infectious wastes such as needles and syringes (Kuo et al., 1999). In addition, high concentrations of Cr were found in plastic wastes from a hospital (Shim et al., 2005). Ti is widely used in medical instruments and implants as a special alloy metal (e.g., substitute for bone). The large amount of Zn in HW ashes may come from a variety of sources. For example, waste plastics and rubber from hospitals are relatively abundant with Zn (Kuo et al., 1999). Also, Zn is widely used in medical adhesive plaster, as well as in the alloys for needle and syringe production (Kuo et al., 1999).

3.3. Sequential extraction results

Fig. 2 shows the sequential extraction results for As, Ba, Cd, Cr, Cu, Mn, Ni, Pb, Sn and Zn in the examined HW ashes. Due to toxicity, these elements have been regulated by the USEPA. Among the elements, As and Cd were only observed in fly ash since only small amounts of them exist in bottom ash, and the amount could not be detected when they were separated into different fractions.

Fig. 2 illustrates that the distribution patterns of various metals in the ashes are quite different. The most abundant species of As is in the form of Fe–Mn oxide, accounting for 43.6–64.2% (103–107 mg kg⁻¹), while the residue form occupies 27.1–29.6% (45–70 mg kg⁻¹). It has been reported that metals associated with the Fe–Mn oxide fraction could not be immediately chemical reactive, but their mobility and availability could be potentially affected by the change of environmental conditions (Tan et al., 1997). Thus, As in HW fly ash may result in potential leaching risk into the environment.

Ba in HW bottom and fly ashes is generally present in the residual fraction (87.8–96.1%, 1203–3332 mg kg⁻¹), while the percentages associated with the exchangeable (0.1–4.0%), carbonate (0.4–2.6%), Fe–Mn oxide (<1.5%) and organic fractions (2.0–4.1%) are relatively low. The residual fraction is generally less mobile, and thus difficult to leach out into the environment. Accordingly, it is believed that Ba in HW ash is relatively safe after landfilling, although the concentration is high in the ash (Tables 2 and 3).

It has been reported that Cd can form relatively volatile compounds with chloride and condense in fly ash in the incineration process; thus it is easy to leach out from the ash under natural conditions (Abanades et al., 2001). The sequential extraction results in this study supported this finding. Fig. 2 shows that approximately 50% of Cd in HW fly ash is concentrated in exchangeable (34.4–51.2%, 27.3–191 mg kg⁻¹) and carbonate fractions (6.6–17.3%, 9.2–36.7 mg kg⁻¹), and 2.2–29.3% (12–15.6 mg kg⁻¹) was observed in the Fe–Mn oxide fraction. These results are consistent with previous studies (Krishnan et al., 1992; Sukandar et al., 2006).

Generally, Cr in both bottom and fly ashes is mainly in the fractions that are relatively difficult to leach out under natural conditions: the Fe–Mn oxide fraction (9.7–16.1%, 3.1–65.4 mg kg⁻¹), organic matter fraction (4.1–12.7%, 4.0–25.4 mg kg⁻¹) and residual fraction (76.4–84.7%, 24.1–527 mg kg⁻¹). A relatively small amount of Cr exists in the exchangeable fraction (0.1–2.8%) or the carbonate fraction (0.5–1.9%).

Most of the organic matter was oxidized during the incineration process. Therefore, it is considered that metals bound to this fraction are relatively low. However, it can be seen from Fig. 2 that Cu is quite abundant in the organic matter fraction (21.8–60.1%, 133–832 mg kg⁻¹). Among the ash samples, fly ashes contain significantly higher amounts of exchangeable and carbonate fractions than bottom ashes, indicating that Cu in HW fly ashes has more mobility than Cu in bottom ashes. Moreover, previous studies have shown that Cu oxides have catalytic effects in the formation of organic pollutants such as PCDDs and PCDFs (Chang and Chung, 1998; Hatanaka et al.,

Table 6
Comparison of heavy metal concentrations in the HW ashes and the MSW ashes (mg kg⁻¹)

	Bottom ash				Fly ash			
	MSW		HW		MSW		HW	
	Average	Range	Average	Range	Average	Range	Average	Range
Ag	1	0.57–1.6	8.4	2.1–24.2	20.4	11.8–29	113	40.5–222
As	5.8	0–93.0	27.8	4.9–50.9	49.2	0.5–37	170	69.3–237
Bi	1.5	0.85–2.6	103	13.2–489	ND	ND	165	38.9–275
Cd	14.1	8.2–31.2	5.3	1.4–10.2	132	0.3–573	237	29.0–635
Co	17.1	3.9–44.1	22.7	10.4–49.9	23.8	14–36.9	5.4	0.58–23.8
Cr	244	44.0–358	397	34.4–895	210	62–1170	65.2	3.5–264
Cu	2824	1169–5251	487	68–2330	678	316–10,600	1702	420–2907
Ni	279	140–710	111	10.7–667	62.4	0–186	36.0	20.0–57.3
Pb	966	430–1626	795	68–2107	2883	223–79,500	3544	900–5363
Sn	354	29.5–276	285	170–406	1836	0–5880	1149	592–1660
Ti	328	182–620	6095	1754–15,518	NT	NT	1940	92–8937
Zn	4510	2866–9601	11,965	2571–30,706	7656	400–207,000	78,686	28,775–121,411

ND: not detected; NT: not tested.

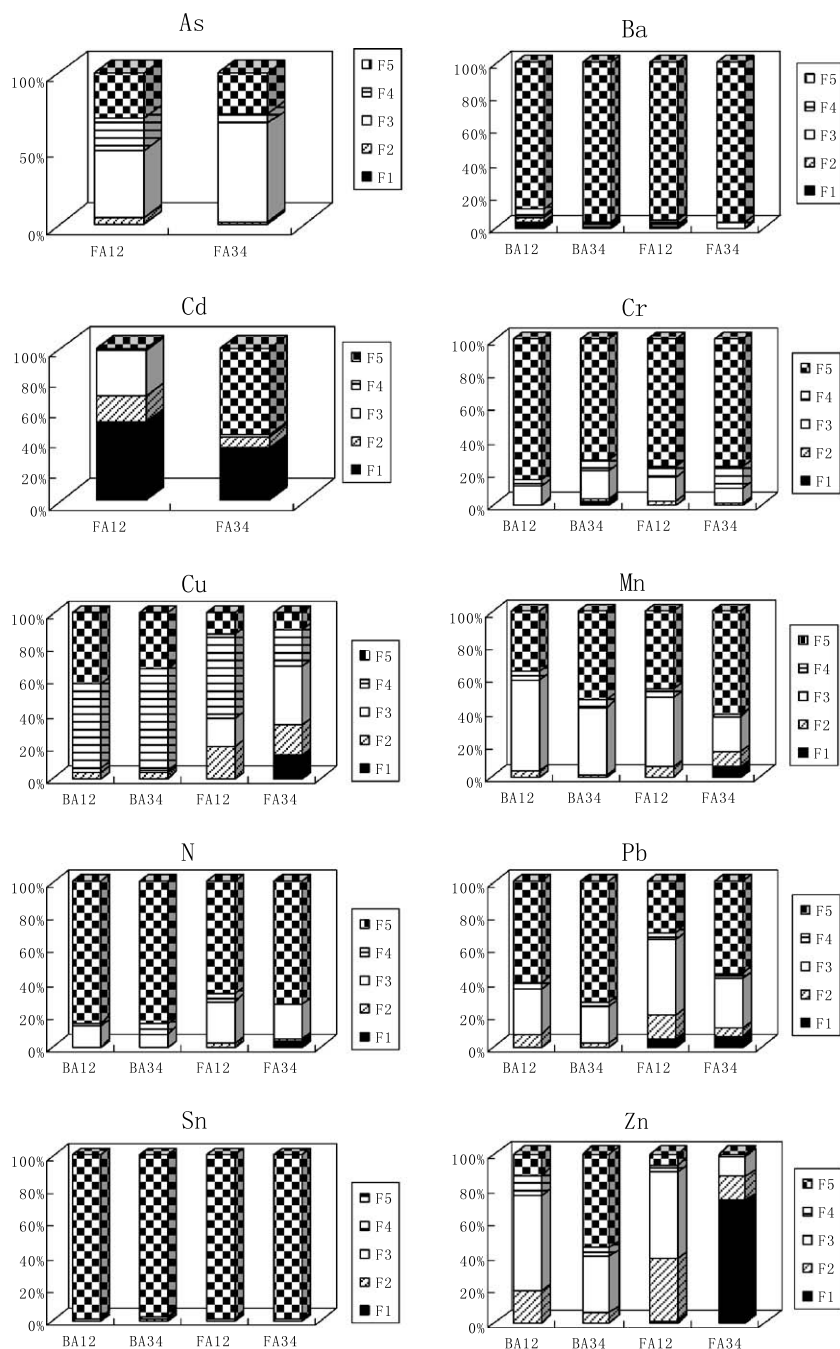


Fig. 2. Fraction distribution of various heavy metals in the HW ashes. F1: Exchangeable; F2: carbonate; F3: Fe–Mn oxide; F4: organic matter; F5: residue fraction. *Average values of duplicate samples from different incinerators were reported, in which BA12 is average of BA1 and BA2, BA34 is average of BA3 and BA4, FA12 is average of FA1 and FA2, FA34 is average of FA3 and FA4.

2004). This viewpoint supports the high amount of Cu occurring in the organic matter fraction in this study.

Mn mainly exists in the Fe–Mn oxide fraction (20.9–54.7%, 76.9–831 mg kg⁻¹), while the residual fraction is 36.4–62.2% (229–1083 mg kg⁻¹). The percentages of Mn associated with the exchangeable (0–6.2%), carbonate (1.3–9.9%) and organic fractions (0.8–5.3%) are relatively low.

Ni mainly concentrates in the residual fraction (67.1–85.9%, 29.9–496 mg kg⁻¹) and Fe–Mn oxide fraction (8.0–24.9%, 2.8–73.2 mg kg⁻¹). The exchangeable and carbonate fractions account for only 0–3.5% and 0.4–2.9%, respectively. Comparatively, Ni in fly ashes has higher amounts of exchangeable, carbonate and Fe–Mn oxide fractions than in the bottom ashes, indicating that Ni in fly ashes has a higher potential to be released into the environment.

Significant amounts of Pb are associated with the residual fraction (30.4–72.6%, 122–4244 mg kg⁻¹) and Fe–Mn oxide fraction (21.3–44.9%, 52.9–2347 mg kg⁻¹). Generally, only a small amount of Pb presents in exchangeable, carbonate and organic fractions, in the range of 0–7.1%, 2.8–14.7% and 2.8–4.9%, respectively. Compared to bottom ashes, fly ashes contain more carbonate and exchangeable Pb, showing that Pb in fly ash is more mobile.

Most of Sn in the HW ash samples is in the residual fraction, accounting for 97.4–98.9% (77.3–1427 mg kg⁻¹). Therefore, although high concentrations of Sn were detected in the ash samples, it has limited environmental availability.

The distribution patterns of Zn in bottom and fly ashes are quite different. In the bottom ashes, large amounts of Zn presents in the Fe–Mn oxide fraction (33.2–57.2%, 3636–4064 mg kg⁻¹) and

the carbonate fraction (6.1–18.2%, 671–1289 mg kg⁻¹). In the fly ashes, Zn mainly is present in the exchangeable (1.3–72.4%, 274–76,040 mg kg⁻¹), carbonate (13.9–36.9%, 7509–14,603 mg kg⁻¹) and Fe–Mn oxide fractions (12.0–50.6%, 10,296–12,979 mg kg⁻¹), while Zn in the organic matter (1.2–5.0%, 1008–1285 mg kg⁻¹) and residue fraction (0.11–6.3%, 120–1279 mg kg⁻¹) is very low. This indicates that Zn present in fly ash may pose a leaching potential to the environment.

During incineration, the mechanisms governing the fate of metals, including nucleating, condensing and coagulating aerosol, are extremely complex. In the case of MSW, it has been reported that the vapor phase of Cd, Pb, Zn, and As transferred into fly ash by nucleation and deposition and most of them existed in the form of metallic or metal oxide, which was easily soluble (Langton, 1989; William and Wendt, 1993). Based on the results obtained in the current study, the following mechanisms governing metal speciation could be deduced:

Ba, Cr, Ni and Sn, with high boiling points, were mainly transferred into the bottom ash, with only small amounts carried into the gaseous phase. These metals were observed both in the bottom and fly ash samples and did not easily react during the incineration process, and thus were mainly found in the stable matrices (residue fraction). As, Cd, Pb, and Zn, with lower boiling points, could easily volatilize into flue gas at higher temperatures and condense on the surface of the fly ash resulting in the formation of compounds that can leach. On the other hand, the species of Cu were quite different from other metals. High Cu content in the organic matter fraction could be attributed to the fact that Cu had catalytic effect in the formation of organic pollutants, e.g., PCDD/DF (Chang and Chung, 1998; Hatanaka et al., 2004), and thus was typically found with the organic fraction of the ash samples.

3.4. TCLP tests

Table 7 presents the TCLP leaching results. It was observed that both Cd and Pb in the leachate of the eight fly ash samples exceeded the USEPA regulatory limits by 2.9 to 50 times and 1.1 to 38 times, respectively. Cu leaching from FA3, FA4, FA5, and FA8

Table 7
Leaching amount of heavy metals from various HW ashes using USEPA extraction procedure (TCLP) (mg l⁻¹)

	As	Ba	Cd	Cr	Cu	Ni	Pb	Zn
BA1	ND	0.92	0.56	3.9	4.8	2.3	0.54	207
BA2	ND	1.3	0.04	0.01	1.4	0.29	0.02	52.3
BA3	ND	0.98	0.05	1.5	0.40	0.03	0.33	80.0
BA4	ND	2.2	0.01	1.5	ND	ND	0.02	13.0
BA5	ND	1.2	0.65	0.25	0.17	0.09	1.8	873
BA6	ND	0.87	0.07	1.8	0.91	0.05	0.78	353
BA7	ND	1.5	0.04	0.69	2.8	0.36	1.8	223
BA8	ND	1.2	ND	ND	ND	ND	0.07	22.6
BA9	ND	1.3	ND	10.5	ND	0.01	0.05	38.8
BA10	ND	1.8	ND	0.01	ND	ND	0.13	12.9
BA11	ND	1.2	0.16	0.23	0.15	0.12	1.8	392
BA12	ND	0.46	0.04	0.04	ND	0.03	0.40	514
BA13	ND	1.3	0.10	0.06	0.51	0.04	0.23	96.9
BA14	ND	1.9	ND	0.07	ND	ND	ND	0.99
FA1	0.39	0.18	3.2	0.21	8.2	0.35	31.6	653
FA2	0.19	0.38	2.9	0.44	6.7	0.56	5.4	544
FA3	0.19	0.06	49.7	0.37	189	1.4	142	1103
FA4	0.32	0.05	42.2	0.26	178	1.4	191	1072
FA5	0.33	ND	23.7	0.06	119	1.9	120	1775
FA6	0.13	0.06	9.4	ND	3.9	0.55	39.8	1498
FA7	0.22	0.07	7.3	ND	0.26	0.33	18.2	1105
FA8	0.20	ND	19.9	0.07	164	2.2	156	1914
US EPA	5.0	100	1.0	5.0	100	100	5.0	NS
Standard								

ND: not detected; NS: not stated in regulation.

also exceeded the regulated level. These results were consistent with the results obtained in the sequential extraction tests. Therefore, the fly ashes should be categorized as hazardous wastes that need strict management and disposal. Comparatively, the bottom ashes generally cause less environmental concern, except that the amount of Cr leached from BA9 exceeded the regulatory value. A further investigation on BA9 showed that the raw material of this sample contained an abundant amount of broken pinheads, which may contribute to the high TCLP leaching result for Cr, since pinheads are made from alloys containing Cr. Therefore, separate collection of metallic items, such as pinheads, from HW could be extremely important to reduce the environmental impact of ashes.

4. Conclusions

Based on the results obtained in this study, HW ashes are a special type of wastes containing relatively large amounts of heavy metals, which make these ashes different from traditional MSW ashes. The concentrations of some toxic heavy metals, such as Ag, As, Bi, Cu, Cd, Cr, Ni, Pb, and Zn, in HW ashes, especially in fly ashes, are significantly higher compared to MSW ashes. Among the heavy metals, more than 50% of Cd is concentrated in the exchangeable fraction thus is highly mobile, and As, Mn, Zn and Pb are abundant in Fe–Mn oxide fraction. The dominant fractions of Ba, Cr, Ni and Sn are in residual fraction, and Cu is mainly bound to organic matter. TCLP results indicated that Cd, Pb, Cu and Zn in HW fly ashes have high mobility and their leaching amounts exceeded the USEPA regulatory values; thus HW fly ashes should be properly treated before landfilling to avoid contamination of the environment. Comparatively, HW bottom ashes generally caused less environmental concerns, with only one sample exceeding TCLP guidelines in Cr leaching potential.

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